Unit-III + IV

(*) write down the limitations of Bhor's model of atom?

→ the limitation's of Bhor's model of atom are given below —

(i) Bhor's model of atom is only valid for single electron system like H, $Li^{++}$, $He^{+}$ etc. for many electron system like Na, Mg Bhor's model of atom is not applicable.

(ii) the velocity of electron in the orbit of an atom is compareable to the velocity of light in valume. so, the mass of the electron changes with the velocity. But in Bhor's model of atom we consider the electron mass is const.

(iii) In Bhor's model of atom it was considered that the mass of the nucleus is infinite as compared to mass of the electron, i.e. there is no motion of nucleous w.r. to electron.

But in real situation the mass of the nucleous is finite and it has a motion w.r.to electron. that is why finite mass correction is necessary in bhor's model of atom.

(iv) By using Bhor's model of atom we cannot able to Explaine different physical phenomena like Zeemann effect, stark effect is related to Spectra of an atom.

(v) By using Bhor's model of atom we cannot able to explaine selection rule related to transition of electron from one state to other state.

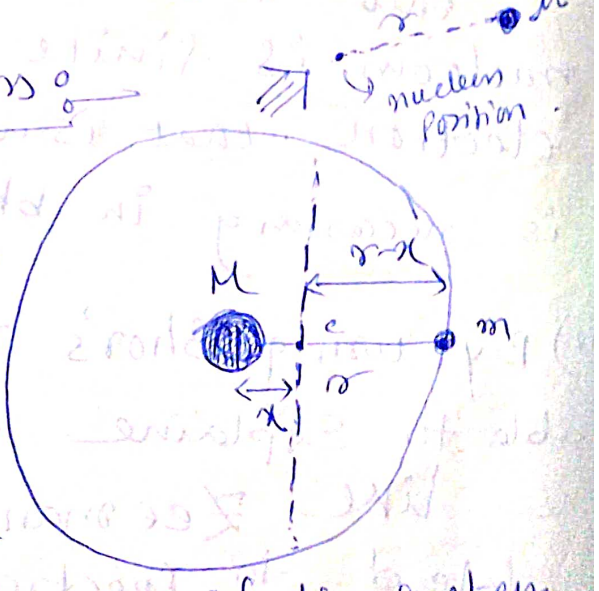
(*) (i) Write down the importance of reduce mass correction / finite mass correction in Bhor's model of atom?

(ii) Find an expression for reduce mass in an 1-$e^-$ system or Bhor's model of atom.

→ (i) → ~~Kinetic~~ In Bhor's model of atom it is considered that the mass of the nucleus is infinite as compared to the mass of the electron, i.e. there is no motion of nucleus w.r.to electron.

But in real situation the mass of the nucleus is finite and it has a motion w.r.to electron. That is why mass correction is necessary in bhor's model.

(ii) Expression for reduce mass :-




We consider an electron revolving arround a nucleus in an orbit of radius 'r'.

M = Mass of the nucleus.

m = " " " electron.

Let, c is the centre of Mass of the system

$x$ = distance of nucleus from centre of mass.

$r - x$ = " " electron " " " "

We know that moment of mass about COM is always zero.

$$Mx = m(r-x)$$

$$\Rightarrow x = \frac{mr}{M+m}$$

Moment of inertia of real system about COM, $I = Mx^2 + m(r-x)^2$

$$= \frac{Mm^2r^2}{(M+m)^2} + m\left\{r - \frac{mr}{M+m}\right\}^2$$

$$= \frac{Mm^2r^2}{(M+m)^2} + \frac{M^2mr^2}{(M+m)^2}$$

$$= \frac{Mmr^2}{(M+m)}$$

$$\boxed{I = \mu r^2} \qquad \mu = \frac{Mm}{M+m} \longrightarrow (1)$$

$\mu$ = reduce mass

By using the concept of reduce mass we can convert a two body system to a one body system.

From's Bhor's model the energy of electron in nth orbit,

$$E_n = -\frac{me^4}{8\varepsilon_0^2 h^2} \cdot \frac{Z^2}{n^2} = -\frac{13.6\, Z^2}{n^2} \text{ eV}.$$

After reduce mass correction the energy of electron in the nth orbit of ~~elect~~ atom

$$E_n' = \frac{-\mu e^4}{8\pi E_0^2 h^2} \frac{Z^2}{n^2}$$

$$= \frac{-me^4}{8\pi \epsilon_0^2 h^2 \left(1+\frac{m}{M}\right)} \frac{Z^2}{n^2}$$

$$\boxed{E_n' = \frac{E_n}{\left(1+\frac{m}{M}\right)}} = -\frac{1}{1+\frac{m}{M}} \frac{13.6 \times Z^2}{n^2} \text{ eV} \quad \text{(iii)}$$

equ$^n$ (iii) is the corrected expression for energy of an electron in nth orbit of an atom.

(*) Find the correction in ground state energy of hydrogen atom due to reduce mass correction?

→ from bhor's model ground state energy of Hydrogen atom.

$$E_1 = -13.6 \text{ eV}, \quad Z = 1, \; n = 1$$

After reduce mass correction ground state energy, of Hydrogen atom,

$$E_1' = \frac{-13.6}{1+\frac{m}{M}} \qquad \frac{m}{M} = \frac{m_e}{m_p} = \frac{1}{1837}$$

$$= \frac{-13.6}{1+\frac{1}{1837}} = -13.5926 \text{ eV}$$

the amount of change in ground state energy

$$\Delta E = E_1' - E_1$$

$$= (-13.5926 + 13.6)\,eV$$

$$= 0.0074\ eV.$$

(*) Show that, in Bohr's theory, if we assume the mass of nucleus ($M$) is finite in comparison with mass of electron ($m$), then Rydberg const. becomes, $R_M = \frac{R_\infty}{1 + \frac{m}{M}}$

$R_\infty$ = Rydberg const. from Bhor's model of atom.

→ Reduce mass correction last question upto equⁿ no — (I).

from Bhor's model - Rydberg const.

$$R_\infty = \frac{me^4}{8\varepsilon_0^2 h^3 c} \longrightarrow (II).$$

after reduce mass correction,

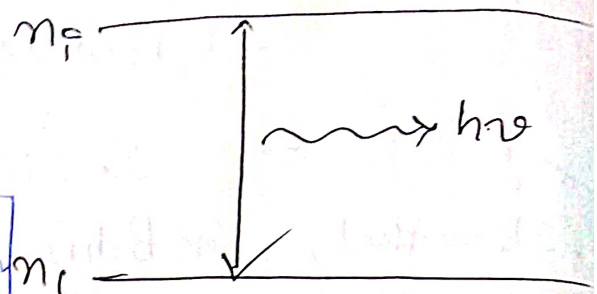
$$R_M = \frac{\mu e^4}{8\varepsilon_0^2 h^3 c} \quad ; \quad \mu = \frac{mM}{M+m}$$

$$= \frac{me^4}{8\varepsilon_0^2 h^3 c\left(1 + \frac{m}{M}\right)} \qquad = \frac{m}{\frac{m}{M} + 1}$$

$$\boxed{R_M = \frac{R_\infty}{1 + \frac{m}{M}}}$$

(iii) Using Reduce mass correction compare between Hydrogen spectra and dutron spectra

→




$$h\nu = E_i - E_f$$

$$\Rightarrow \frac{hc}{\lambda} = \frac{me^4}{8\pi\epsilon_0^2 h^2 (1+\frac{m}{M})}\left[\frac{1}{n_f^2}-\frac{1}{n_i^2}\right] n_f$$

for, $Z = 1$

$$\Rightarrow \frac{1}{\lambda} = \frac{me^4}{8\pi\epsilon_0^2 h^3 c}\cdot\frac{1}{(1+\frac{m}{M})}\left[\frac{1}{n_f^2}-\frac{1}{n_i^2}\right]$$

$$\Rightarrow \frac{1}{\lambda} = \frac{R_\infty}{1+\frac{m}{M}}\left[\frac{1}{n_f^2}-\frac{1}{n_i^2}\right], \quad R_\infty = \frac{me^4}{8\pi\epsilon_0^2 h^3 c}$$

→ (i)

For Hydrogen spectra.

$$\frac{1}{\lambda_H} = \frac{R_\infty}{1+\frac{m_e}{m_p}}\left[\frac{1}{n_f^2}-\frac{1}{n_i^2}\right] \longrightarrow (ii)$$

for, dutron spectra,

$$\frac{1}{\lambda_D} = \frac{R_\infty}{1+\frac{m_e}{2m_p}}\left[\frac{1}{n_f^2}-\frac{1}{n_i^2}\right] \longrightarrow (iii).$$

(i) $\frac{0}{0}$ (iii) $\Rightarrow$

$$\frac{\lambda_D}{\lambda_H} = \frac{1+\frac{m_e}{2m_p}}{1+\frac{m_e}{m_p}}$$

$$\Rightarrow \boxed{\frac{\lambda_D}{\lambda_H} = 0.9997} \longrightarrow (iv).$$

equ'(iv) represent, the ratio of wave length of Dutron's spectra and to Hydrogen spectra for specific transition of electron.

(*) Find magnetic moment for an electron motion in a orbit of an atom.

→ We consider an electron revolving around the nucleus in an orbit of radius $r$.

we know that a moving electron is equivalent to current,

$$I = \frac{-e}{T} = \frac{-e}{\frac{2\pi}{\omega}} = \frac{-e\omega}{2\pi}, \text{ here,}$$

T = Time Period of revolution $= \frac{2\pi}{\omega}$

The magnetic moment corresponding to electron motion.

$\mu$ = Current × area enclosed by the current

$$= I \times \pi r^2$$

$$= -\frac{e\omega}{2\pi} \times \pi r^2$$

$$= -\frac{e}{2m} mwr^2, \text{ Here, } m = \text{mass of electron}$$

$$\mu = -\frac{e}{2m} L, \text{ Here, } L = mwr^2 = \text{angular momentum of the electron}$$

In vector notation.

$$\boxed{\vec{\mu} = -\frac{e}{2m}\vec{L}}$$

$$\boxed{\vec{\mu} = -\frac{e}{2m}\vec{L}} \longrightarrow (1)$$

the -ve sign indicate that the direcⁿ of magnetic moment and angular momentum is opposite in direcⁿ.

In the figure, angular momentum outward from the paper and magnetic moment inward to the paper.

Again, we know that, $L = \sqrt{l(l+1)}\,\hbar$

from equⁿ $\longrightarrow$ (1).

$$\therefore \mu = -\frac{e\hbar}{2m}\sqrt{l(l+1)}$$

$$\Rightarrow \boxed{\mu = -\mu_B\sqrt{l(l+1)}}, \quad \mu_B = \frac{e\hbar}{2m}$$

$l$ = orbital Quantum number = azimuthal Q. M. no.

$= 9.27 \times 10^{-24}$ J/T or Amp/m

Here, $\mu_B = \frac{e\hbar}{2m}$ is known as = Bohr magneton.

Bohr magneton.

It is one of the smallest unit of magnetic moment used to measure magnetic moment of microscopic particle's or atoms.

Note:- $\mu = -\mu_B\sqrt{l(l+1)}$ is known as orbital magnetic moment.

(*) Find the orbital magnetic moment of Cl (Clorine)

$\rightarrow$ $Cl^{17} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$ 1 1 1

There is only one unpaired electron in p orbital.

$l = 1$

$\mu = -\mu_B \sqrt{2}$

$= -\sqrt{2}\mu_B$ , where,

$\mu_B = 9.27 \times 10^{-24} J/T$

Note:- the chemical chereetaristic and the Spectra chereetaristic of an atom depends on the unpaired $e^-$ present in the atom.

Due to the magnetic moment of electron, an atom can be considered as tiny magne

(*) Define Larmor precession. Find an expression for Larmor frequency of Precession.

→ when an atom is placed in an external Magnetic field, the orbit precesses about the direction of applied Magnetic field. Due to the torque applied on the atom, this Precession is known as Larmor Precession and the frequency of this Precession is known as larmor frequency

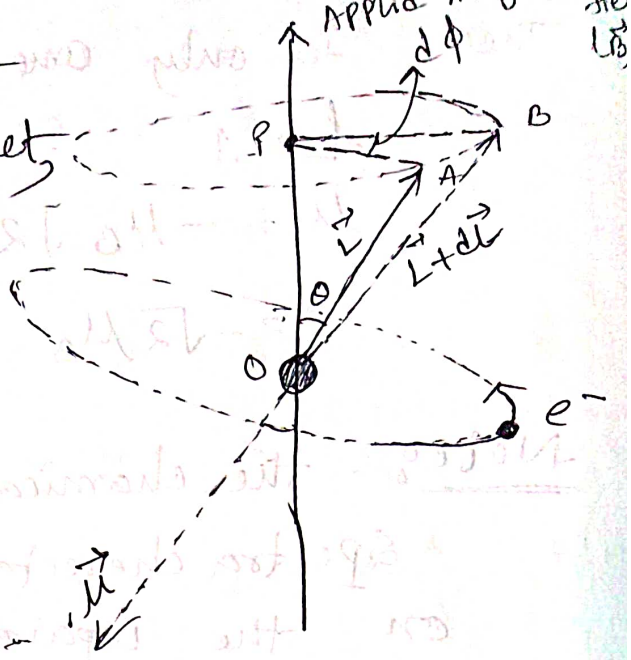
Expression for Larmor frequency

Here $\vec{l}$ = angular momentum of the electron.

$\vec{\mu}$ = magnetic moment of the electron corresponding to orbital motion.

$\vec{B}$ = applied magnetic field / external magnetic field.

We know that an atom behave as a tiny magnet, that is why a torque will be applied on the atom.




$$\text{Torque}(\vec{\tau}) = \vec{\mu} \times \vec{B}$$

$$|\vec{\tau}| = |\vec{\mu} \times \vec{B}|$$

$$= \mu B \sin(\pi - \theta)$$

$$= \mu B \sin\theta \longrightarrow (1)$$

again $\text{torque}(\vec{\tau}) = \frac{d\vec{L}}{dt}$

at Point 'A' the angular momentum is $\vec{L}$,

at Point 'B' angular momentum is $\vec{L} + d\vec{L}$

Let, at time dt angular momentum change by $d\vec{L}$.

from $\triangle OPA$, $\sin\theta = \frac{PA}{OA}$ $\Rightarrow PA = OA \sin\theta$

$PA = L\sin\theta \longrightarrow$

let, $\omega$ is the angular frequency of Precession of angular momentum about the direction of applied magnetic field.

again, $d\phi = \omega\, dt$

$$\Rightarrow \frac{AB}{PA} = \omega dt$$

$$\Rightarrow \frac{dL}{L\sin\theta} = \omega\, dt$$

$$\Rightarrow \frac{dL}{dt} = L\omega\sin\theta$$

$\Rightarrow \tau = \omega L \sin\theta$.

$\Rightarrow \mu B \sin\theta = \omega L \sin\theta$. [unit eqn - (1)]

$\Rightarrow \omega = \frac{\mu B}{L}$ ——— (III)

again we know that, $\vec{\mu} = -\frac{e}{2m}\vec{L}$

$$|\mu| = \frac{e}{2m} L$$

$$\Rightarrow \frac{\mu}{L} = \frac{e}{2m} \longrightarrow (IV).$$

using (IV) in (III) $\Rightarrow$

$$\omega = \frac{eB}{2m}$$

$$\Rightarrow 2\pi f = \frac{eB}{2m}$$

$$\Rightarrow \boxed{f = \frac{eB}{4\pi m}}$$

this is the expression for Larmor frequency.

(*) write down the features of vector atom model;

(***) (OR)

(**) write down the element's of vector atom model?

(OR)

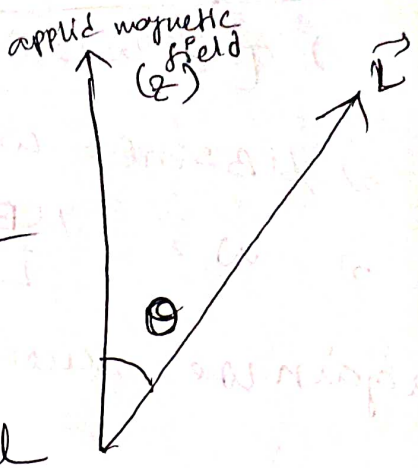
Discuss about vector atom model.

$\longrightarrow$ the main feature's of vector atom model are ———

(a) space quantization : let, Orbital angular momentum of an atom is $\vec{L}$ and corrosponding orbital magnetic moment is $\vec{\mu_L}$ and external magnetic field is allied in the z-direcn as shown in figure.

Here $\theta$ is the angle between applied magnetic field and orbital angular momentum.

$$L = \sqrt{l(l+1)}\,\hbar$$




the z, component of Orbital angular momentum

$$L_z = L\cos\theta \longrightarrow (1)$$

again $L_z = m_l \hbar$, $m_l$ = orbital magnetic quantum no.

$\longrightarrow (11)$

using equⁿ (11) in eq (1) = $-l \ldots\ldots +l$.

$$m_l \hbar = L\cos\theta.$$

$$\Rightarrow \cos\theta = \frac{m_l \hbar}{\sqrt{l(l+1)}\,\hbar}$$

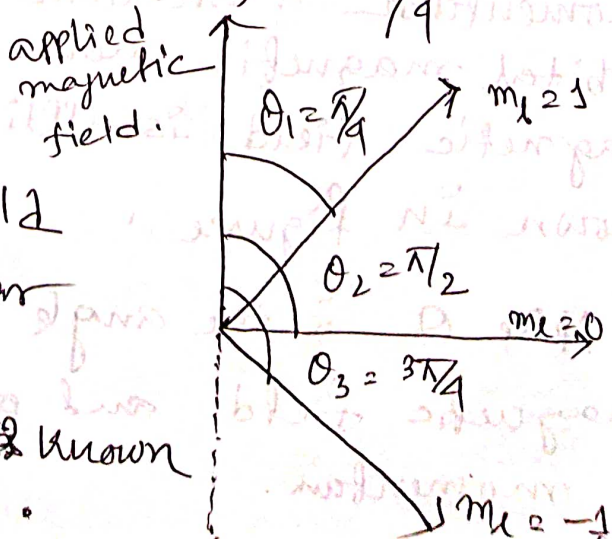
$$\Rightarrow \boxed{\theta = \cos^{-1}\left\{\frac{m_l}{\sqrt{l(l+1)}}\right\}}$$

for example:- in case of P-orbital; $l = 1$, $m_l = -1, 0, 1$

for, $m_l = 1$, $\theta_1 = \cos^{-1}\left\{\frac{1}{\sqrt{2}}\right\} = \pi/4$

$m_l = 0$, $\theta_2 = \cos^{-1}(0) = \pi/2$

$m_l = -1$, $\theta_3 = \cos^{-1}\left(-\frac{1}{\sqrt{2}}\right) = 3\pi/4$




the angle between applied magnetic field and the orbital angular momentum is fixed.

this phenomenone is known as Space Quantization.

similarly, in case of spin angular momentum,

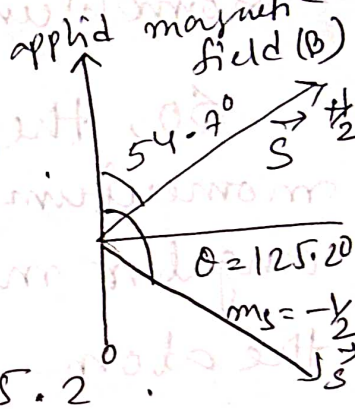
$$S = \sqrt{s(s+1)}\,\hbar \qquad S = \frac{1}{2} \Rightarrow \text{Spin Quantum no.}$$

$$S_z = m_s \hbar \qquad m_s = +\frac{1}{2}, -\frac{1}{2} = \text{spin magnetic Quantum no.}$$

$$\cos\theta = \frac{m_s}{\sqrt{s(s+1)}}$$

for $m_s = +\frac{1}{2}$,

$$\theta_1 = \cos^{-1}\left\{\frac{\frac{1}{2}}{\frac{\sqrt{3}}{2}}\right\} = 54.7^0$$




for $m_s = -\frac{1}{2}$, $\theta_2 = \cos^{-1}\left\{\frac{-\frac{1}{2}}{\frac{\sqrt{3}}{2}}\right\} = 125.2$.

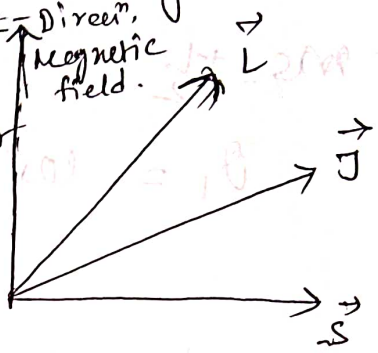
(ii) Electron Spin:- Goudsmith and Uhlenbeck in 1925 published that an electron must be considered as a charged sphere spinning about it's own axis, having an intrinsic (buildin) angular momentum and corrosponding magnetic dipole moment.

the spin magnetic moment of an electron $\vec{\mu_s} = -2\frac{e}{2m}\vec{s}$, whose, $\vec{s}$ = spin angular momentum.

[Experimentally it was proved that, $\frac{\vec{\mu_s}}{\vec{s}}$ is twice of $\frac{\vec{\mu_l}}{\vec{l}}$

(*) i) Write down the concept of coupling of orbital angular momentum and spin angular momentum?
ii) Discuss about L-s coupling and J-J coupling with example.

→ (i) we consider an atom with 1 unpair elec the orbital angular momentum of the electron = $\vec{L}$ and spin angular momentum = $\vec{s}$.




So, the resultant angular momentum or ~~spin~~ total angular momentum of the atom, $\vec{J} = \vec{L} + \vec{s}$

where, $J = \sqrt{j(j+1)}\,\hbar$

$j$ = inner quantum number.

the z component of total angular momentum

$J_z = m_j \hbar$, where, $m_j$ = inner magnetic quantum no.

$= -j \ldots\ldots +j$

from the figure,

$$J_z = L_z + S_z$$

$$\Rightarrow m_j \hbar = m_l \hbar + m_s \hbar$$

$$\Rightarrow \boxed{m_j = m_l + m_s}$$

$\therefore j = |l+s|, \ldots\ldots |l-s|$.

this phenomenone of total angular momentum is known as spin orbital

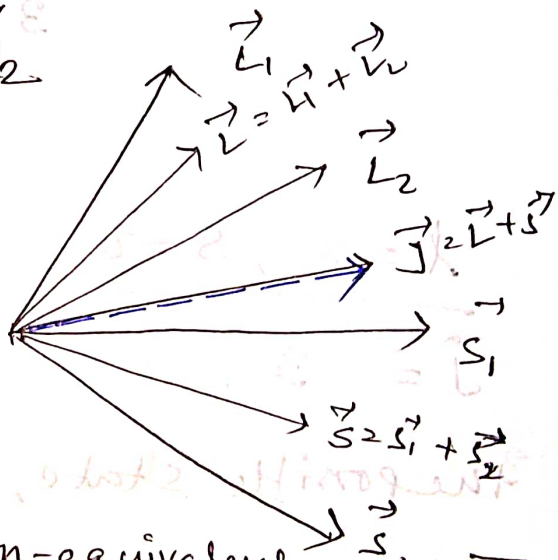
coupling of angular momentum.

(ii) If there is more than one unpaired electron, the system will be much more complicated than single e⁻ system.

there are two types of coupling —

(i) L-S coupling :-

We consider an atom with two unpaired electron, for the 1st electron spin angular momentum $= \vec{S}_1$ and orbital angular momentum $= \vec{L}_1$, for 2nd electron spin angular momentum $= \vec{S}_2$ and orbital angular momentum $= \vec{L}_2$




For example, we consider two unpaired non-equivalent electron

$3p^1, 3d^1$

Here, $l_1 = 1, \quad s_1 = \frac{1}{2}$

$l_2 = 2, \quad s_2 = \frac{1}{2}$

[non-equivalent = electron belongs to different orbital]

orbital-orbital coupling :- $(l_1 - l_2)$

$l_1 = 1, \quad l_2 = 2.$

$\therefore \quad l = |l_1 + l_2| \cdots\cdots |l_1 - l_2|$

$= 3, \quad 2, \quad 1$

## Spin-Spin ($S_1$-$S_2$) coupling :-

$S_1 = \frac{1}{2}$, $S_2 = \frac{1}{2}$

$\therefore S = |S_1 + S_2| \ldots\ldots\ldots |S_1 - S_2|$

$S = 1, \quad , 0$

## L-S coupling :-

$l = 3, \; S = 1$

$\vec{J} = |l+s| \ldots\ldots\ldots |l-s|$

$\Rightarrow \vec{J} = 4, 3, 2$

the possible states, ${}^3F_4, {}^3F_3, {}^3F_2$

### $l = 3, S = 0$

$\vec{J} = 3.$

the posible state, ${}^1F_3$

### $l = 2, S = 1$

$\vec{J} = 3, 2, 1$

Posible states, ${}^3D_3, {}^3D_2, {}^3D_1$

### $l = 2, S = 0$

$\vec{J} = 2.$ Possible state, ${}^1D_2$

### $l = 1, S = 1$ $\vec{J} = 2, 1, 0$

Spectroscopic notation

$l = 0$ . S

$l = 1$ , P

$l = 2$ , D

$l = 3$ , F

$l = 4$ , G

$l = 5$ , H

$l = 6$ , I

$\left[ {}^{2S+1}F_{\vec{J}} \right]$

$2S+1$ (state) $\vec{J}$

Possible state; $^3P_2, ^3P_1, ^3P_0$

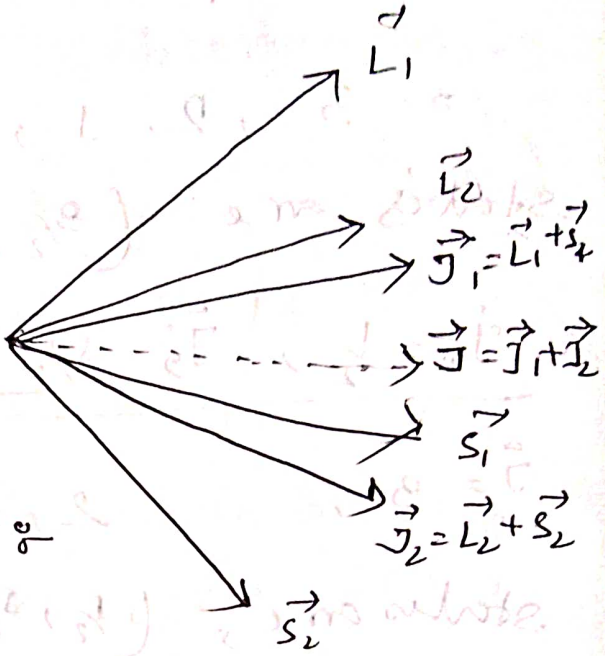
$l = 1, \; s = 0$

$J = 1$ Possible state $^1P_1$

(ii) J-J coupling :-

We consider two unpaired non-equivalent electron

$3p^1 \; 3d^1$




Spin-orbital coupling for (1st $e^-$) :-

$l_1 = 1 \quad s_1 = 1/2$.

$\vec{J}_1 = |l_1 + s_1) \cdots\cdots |l_1 - s_1|$

$J_1 = 3/2, \ldots, 1/2$

Spin-orbital coupling for (2nd $e^-$) :-

$l_2 = 2, \quad s_2 = 1/2$.

$\vec{J}_2 = |l_2 + s_2) \cdots\cdots |l_2 - s_2|$

$J_2 = 5/2, \; 3/2$

J-J coupling :-

$J_1 = 3/2, \quad J_2 = 5/2$.

$\vec{J} = |j_1 + j_2| \ldots |j_1 - j_2|$

$= 4, 3, 2, 1$

States are $(3/2, 5/2)_{4,3,2,1}$.

$\vec{J}_1 = 3/2$, $\vec{J}_2 = 3/2$.

$\vec{J} = |\vec{J}_1 + \vec{J}_2| \ldots\ldots |\vec{J}_1 - \vec{J}_2|$

$= 3, 2, 1, 0$

states are $(3/2, 3/2)_{3,2,1,0}$.

$\vec{J}_1 = 1/2$, $\vec{J}_2 = 5/2$

$\vec{J} = 3, \quad 2$

states are; $(1/2, 5/2)_{3,2}$.

$\vec{J}_1 = 1/2$, $\vec{J}_2 = 3/2$

$\vec{J} = 2, 1$

states are $(1/2, 3/2)_{2,1}$

(*) Find the L-S coupling and J-J coupling between two unpaired $e^-$ $3p^1, 4f^1$

(***) Write down the difference between L-S coupling and J-J coupling?

→

| L-S | J-J |
|---|---|
| (i) In L-S coupling spin-spin interaction and orbital-orbital interaction is graber than s-O interaction | (i) in JJ coupling s-s and O-O interaction is less than s-O interaction |

(ii) L-S coupling is observe in lighter atom's (ex- Na, cal K) etc.

(ii) J-J coupling is observe in hanier atoms like (cu, Fe) etc.

(*) why L-S coupling is observed in lighter atom's when, J-J coupling is observed in hevier atoms?

→ In lighter atom's spin-spin interaction and orbital orbital interaction is greater than spin orbital interaction.

But in heavier atom spin-orbital interaction is greater than spin-spin, orbital-orbital interaction, that's why L-S coupling is observed in lighter atom's and J-J coupling is observed in heavier atom's.

(*)(i) Discuss how stern-Gerlach experiment Proof the space quantization and spin of electron.

(OR)

Set up an experiment for support of vector atom moded.

(ii) Why silver atoms are used in stern-Gerlach experiment?

→ (i) Stern-Gerlach in 1921 Perform an experiment which demonstrated directly that an atom placed in an external

magnetic field can take only certain discreate orientations with respect to the applied magnetic field (space quantization).

It also demonstrated the existance of electron spin, thus providing an experimental Verification of vector atom model. This was the main aim of stern-Gerlach experiment. (aim of this expt.)

The Experimental setup of this Experiment is shown in the below figures

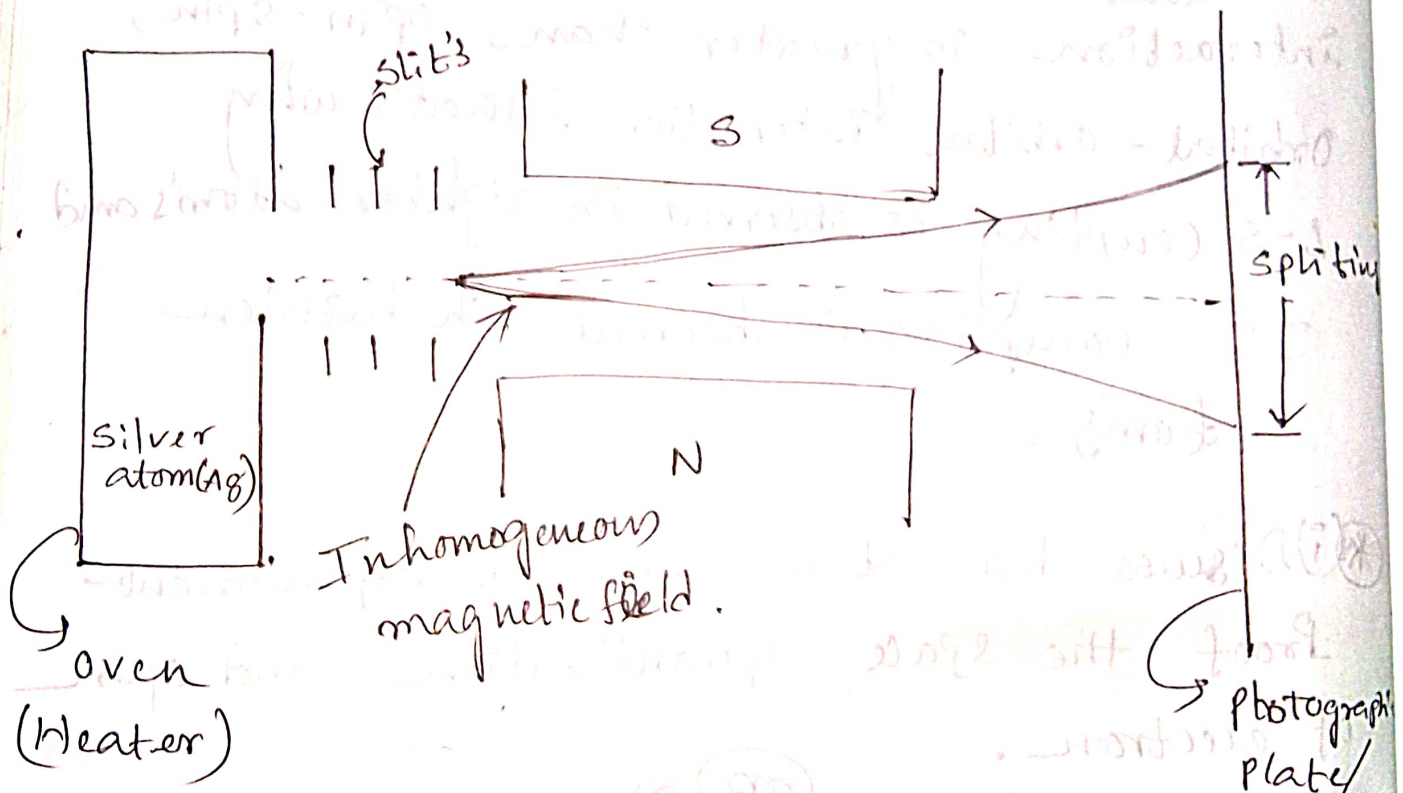



fig:- Expt. set up of Stern Gerlach Expt.

fig:- Creation of inhomogeneous Magnetic field

A Beam of nutral silver atom's was form By heating silver in an oven as shown in the figure. this silver atom's was collimated (send in a particular direc$^{n}$) by a series of slit's, then the silver atom's passed through a inhomogeneous magnetic field.

the magnetic field was produced by specially designed permanent magnet's as shownin fig-2.

the magnetic field intensity change's with distance (inhomogeneous).

A magnetic dipole experience's anet diffletion force in an inhomogeneous magnetic field which depend's on the Orientation of the magnetic dipole in the External magnetic field. we know that atom's behave as a tiny magnet, so they experience's a net diffletion force when passing through the inhomogeneous magnetic field.

If an atom could have any orientation in the External magnetic field then the silver atom beam will split into several component because all type of orientation's are possible. But in stern-gerlach expt.

We only get two component's of silver atom beam in the photographic plate. This showed that the atom's passing through the external magnetic field, where oriented in discreate direcn w.r.to external magnetic field, and the diffleetion of atom in inhomogeneo magnetic field prove the existance of electron spin.

(ii) the atomic no. of silver atom ($Z$) = 47.

the electron configuration of silver atom,

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 4d^{10} 5s^1$

there is only one unpaired electron in sliver atom in the s-orbital, $l=0$, $\vec{L}=0$, $\vec{\mu}_L=0$

where, $l$ = orbital quantum no

$L$ = orbital angular momentum

$\mu_L$ = magnetic moment.

$S=\frac{1}{2}$, $\vec{S}=\sqrt{s(s+1)}\,\hbar$, $\vec{\mu}_s=-2\frac{e}{2m}\vec{S}$

$S$ = spin quantum no.

$\vec{S}$ = spin angular momentum.

$\vec{\mu}_s$ = spin magnetic moment.

$\because l=0$, the orbital magnetic moment of this atom is zero, the magnetic moment of this atom is only due to spin of the electron.

the spin manguetic quantum no. $m_s=\pm\frac{1}{2}$, that's why the silver atom beam split's into two component's.

there is no other atom with one unpa

electron in S-orbital, that has less reactivity than silver. that's why silver atom is used in stern-gerlach expt.

(*) write down the aim of stern-gerlach experiment. → last page.

(*) why inhomogeneous magnetic field is used in stern-gerlach expt?

→ In homogeneous magnetic field the silver atom's (tiny magnet's) would have experienced only pure rotational torque and no deflecting force. In such condition we could not obtain the diffected component's inspite of the orientation's of the silver atom in External magnetic field. that's why we prove electron spin and space quantization inhomogeneous magnetic field is used in stern-gerlach experiment.

(*) why nutral beam of silver atom is used in stern-gerlach expt. but silver ion's are not used in stern-gerlach Experiment?

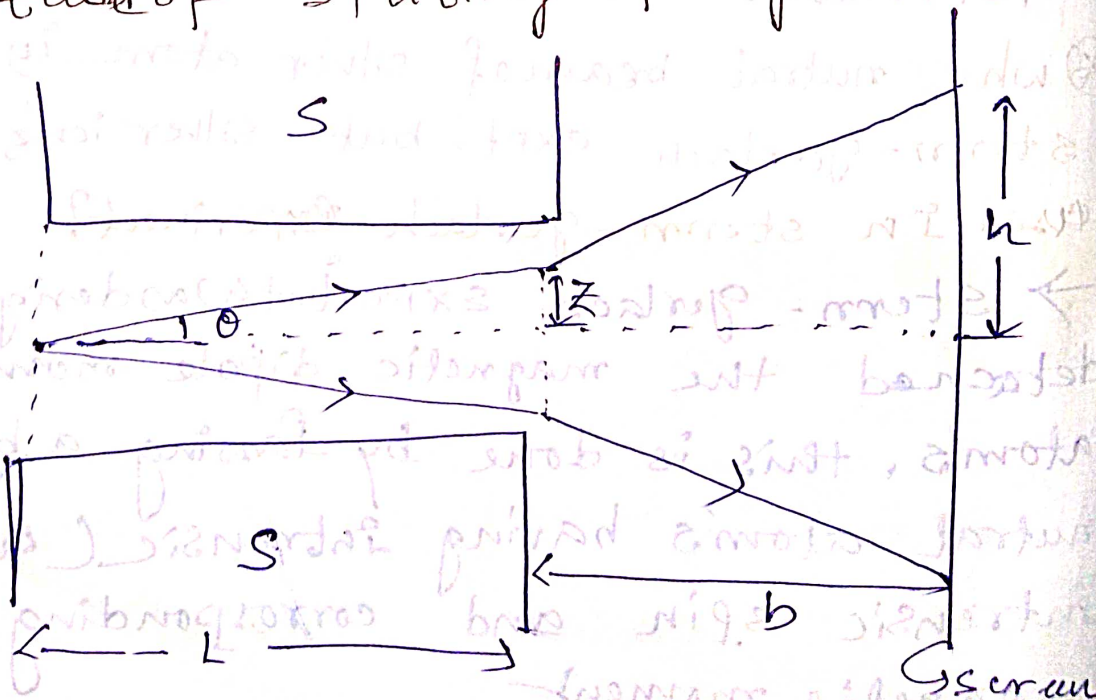
→ stern-gerlach experiment was designed to detached the magnetic dipole moment of atom's. this is done by passing a beam of nutral atom's having intrensic (Build in) intrensic spin and corrosponding spin magnetic moment.

If instant of nutral silver atom's, silver ion's are used, then the moving charged

Ion's will directly interact with external magnetic field, hence deflected from their path due to magnetic force. that's why in this situation we cannot able to detect spin magnetic moment and space quantization, this is why nutral silver atom beam is used but silver ions are not used in stern-gerlach expt.

(*) In a stern-gerlach expt. A beam of silver atom's with velocity 'v' enter's in an inhomogeneous magnetic field with gradient $\frac{\partial \vec{B}}{\partial z}$ (magnetic field change's with z) and the length of the inhomogeneous magnetic field is 'L'. after emerging from inhomogeneous magnetic field they traveled a distance 'b' before reaching the photographic plate or the screen. Find an expression for the magnetic tudd of spliting of Ag atom's?

→



# Vibrational Spectra

(*) (i) Explain the origin of vibrational spectra?
(ii) why vibrational spectra is also known as infrared spectra?

→ (i) when a polar molecule (Net dipole moment is not zero) vibrate the value of dipole moment changes with vibration which create radiation field.

In radiation field, the polar molecule can absorb or radiate electro magnetic radion or photon. This is the origin of vibrational spectra.

Dipole moment- $\mu = \delta \times$ bond length (r)

as the bond length changes with vibration, the value of dipole moment also changes.

(ii) the wave length of radiation absab or radiate vibrational spectra is $10^{-3}$ m → $10^{-5}$ m, which is the range of infrared electromagnetic radiation, this is why vibrational spectra is also known as infrared spectra.

The molecules which are capable of vibrational spectra is known as infrared active.

The molecules which are not capable of vibrational [illegible] infrared inactive.

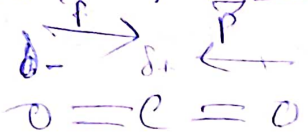
(*) Why Homonuclear molecules are infrared inactive?

→ The dipole moment of Homonuclear molecules is zero, i.e why when Homonuclear molecule vibrates, there is no change in dipole moment and no vibrational spectra will observe. I.e. Homonuclear molecules are infrared inactive.

Ex — $H_2$, $F_2$, $O_2$, $N_2$ etc.

(*) why $CO_2$ is infrared inactive.

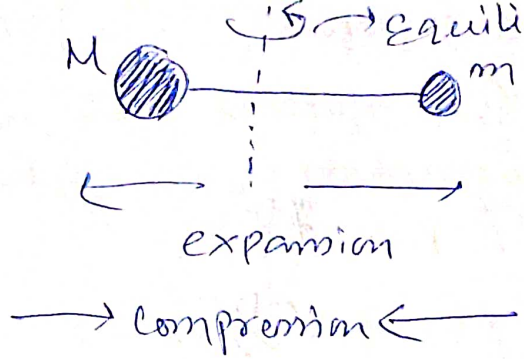
→




The net dipole moment of Homo nuclear molecules for this case $CO_2$ is zero. i.e, when $CO_2$ molecule vibrates, there is no change in dipole moment and no vibrational spectra will observe. i.e., why $CO_2$ is infrared inactive.

(*) Find the vibrational energy levels of a polar molecule vibrates about mean position. Hence show that the vibrational energy levels are equally spaced.

→ we consider a diatomic polar molecule vibrates about there mean position or equilibrium position —




In vibrational spectra the bond length between the atom's act as ideal spring.

The total energy of the system;

$$E = \frac{p^2}{2\mu} + \frac{1}{2}kx^2; \quad \omega = \sqrt{\frac{k}{\mu}} = \text{angular frequency}$$

$$E = \frac{p^2}{2\mu} + \frac{\mu\omega^2 x^{2n}}{2}$$

$\mu$ = reduce mass of the system.

To find the vibrational energy level's we have to solve, schrodinger equⁿ,

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega, \qquad n = 0, 1, 2, \ldots$$

= vibrational quantum no.

The energy levels interm's of wave no.

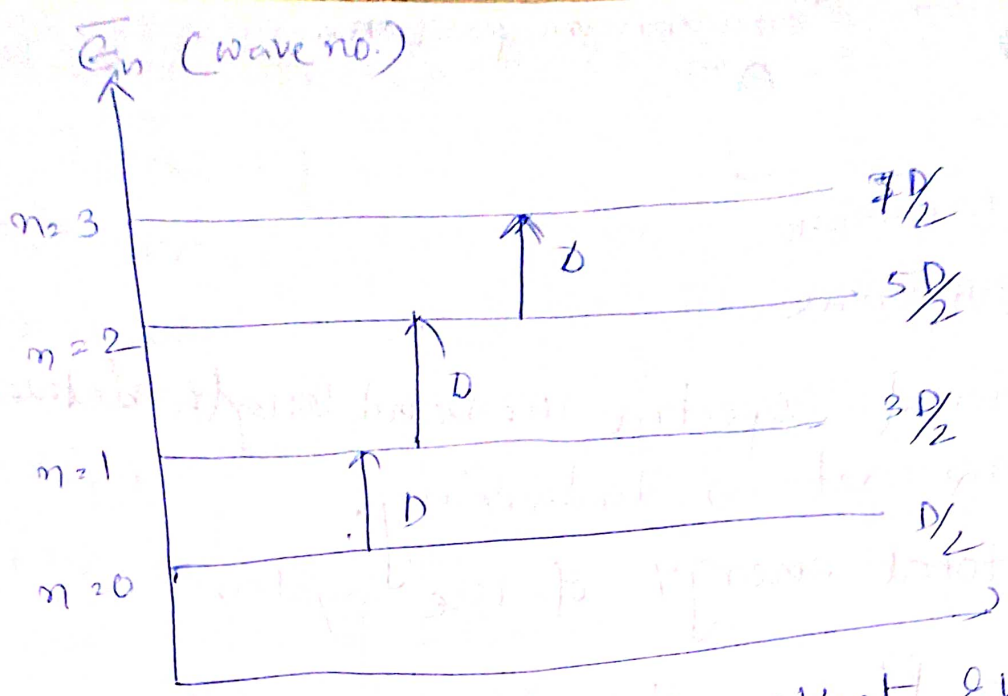
$$\bar{\epsilon}_n = \frac{E_n}{hc} = \frac{\left(n+\frac{1}{2}\right)\hbar\omega}{hc}$$

$$= \frac{\omega}{2\pi c}\left(n+\frac{1}{2}\right)$$

$$= \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}\left(n+\frac{1}{2}\right)$$

$$\bar{\epsilon}_n = D\left(n+\frac{1}{2}\right), \text{ where, } D = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

= vibrational const.




From the figure it is clear that energy level's of vibrational spectra is equally spaced and the spacing between consiquitive energy level is D in terms of wave no.

(*) Discuss the effect of isotopic substitution in vibrational spectra?

→ We consider a polar molecule $H^1Cl^{35}$, as $H^1Cl^{35}$ is a polar molecule it exicute rotational spectra.

Let, $H^1$ is replaced by it's stable isotope $H^2$ then the molecule is become $H^2Cl^{35}$

Now we have to find the change in vivrational spectra due to isotropic substitution.

As the electronic configuration of $H^1$ and $H^2$ is same, the bond langth remain const. As the mass of $H^1$ and $H^2$ are not same, reduce

mass of HCl changes and corresponding Moment of Inertia also changes. Due to change in Moment of Inertia → the rotational const. also changes..

The reduce mass of $H^1Cl^{35}$ is $\mu_1 = \frac{35}{36}$ amu.

the reduce " " $H^2Cl^{35}$ is $\mu_2 = \frac{70}{37}$ amu.

$\therefore \mu_2 > \mu_1$

⊛ vibrational const. $D = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$.

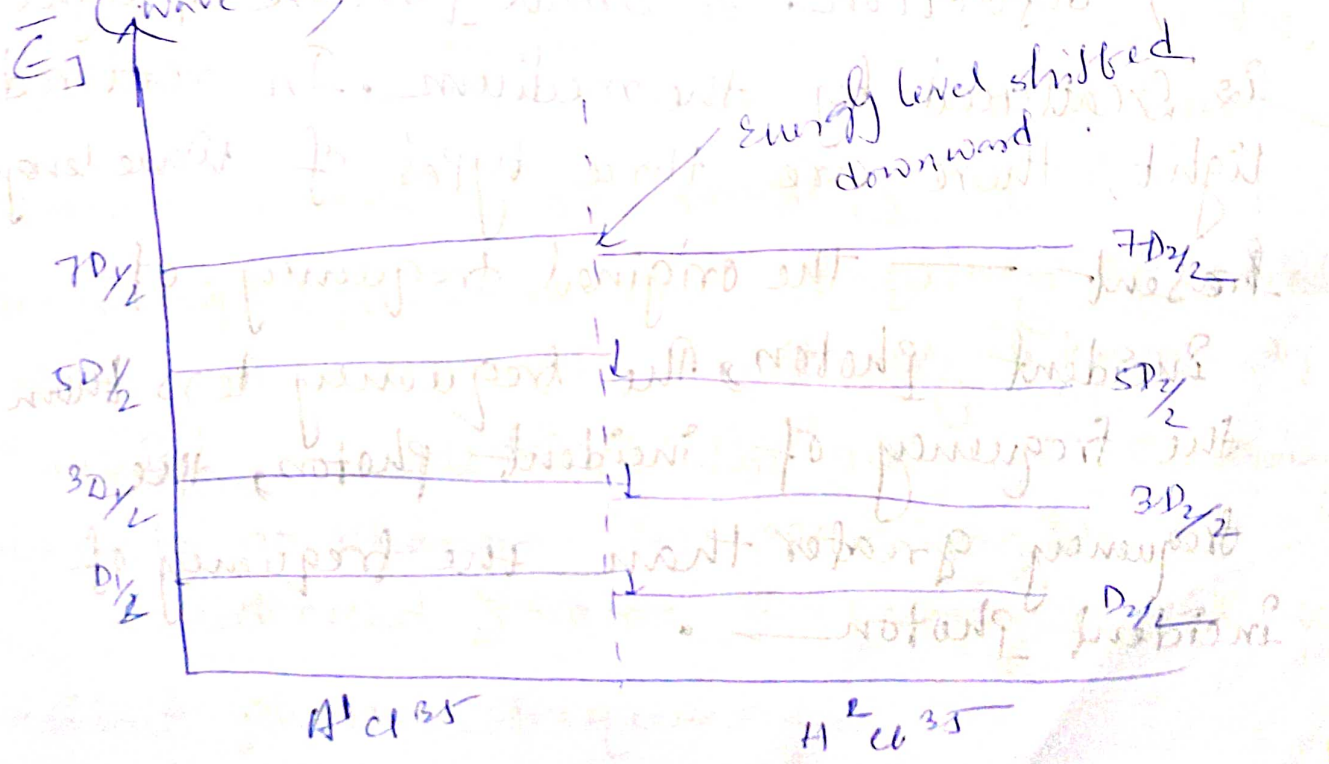
$\therefore \frac{D_2}{D_1} = \sqrt{\frac{\mu_2}{\mu_1}}$

$D_1$ = vibrational const. of $H^1Cl^{35}$

$D_2$ = " " " $H^2Cl^{35}$

$\because \mu_2 > \mu_1$ ; $D_1 > D_2$

Due to, isotopic substitution → vibrational const. Decreases and the vibrational energy level will shifted downwards.

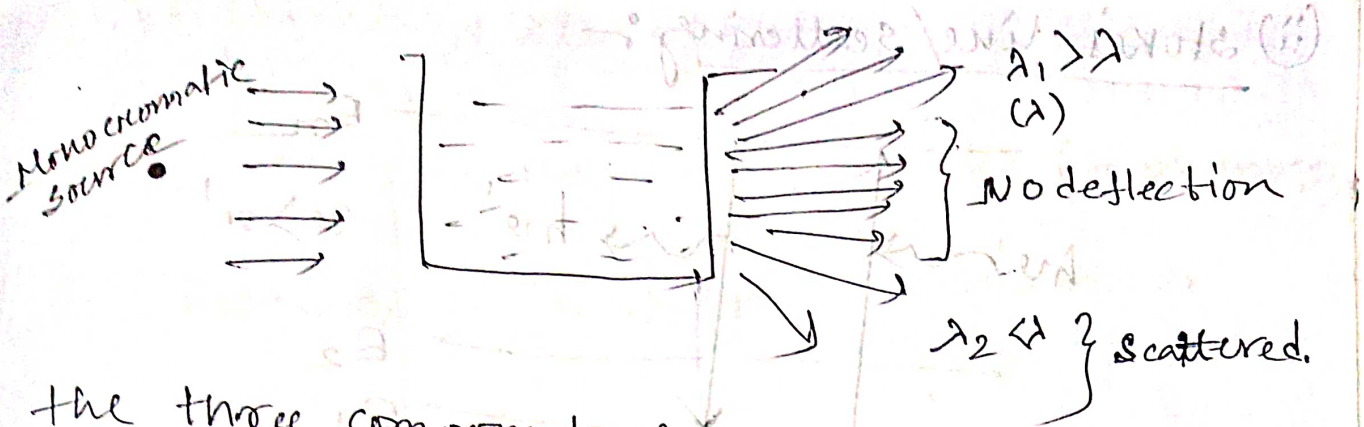


(A) (i) What do you mean by raman effect?
(ii) Write down the use of raman effect?

→ (i) The raman effect is the process of scattering of light or photons by molecules of a medium. The scattering occurs due to achange in the wave length of light as it enters the medium. There are two types of scattering in raman effect. one is stokes line and other is anti stokes lines.

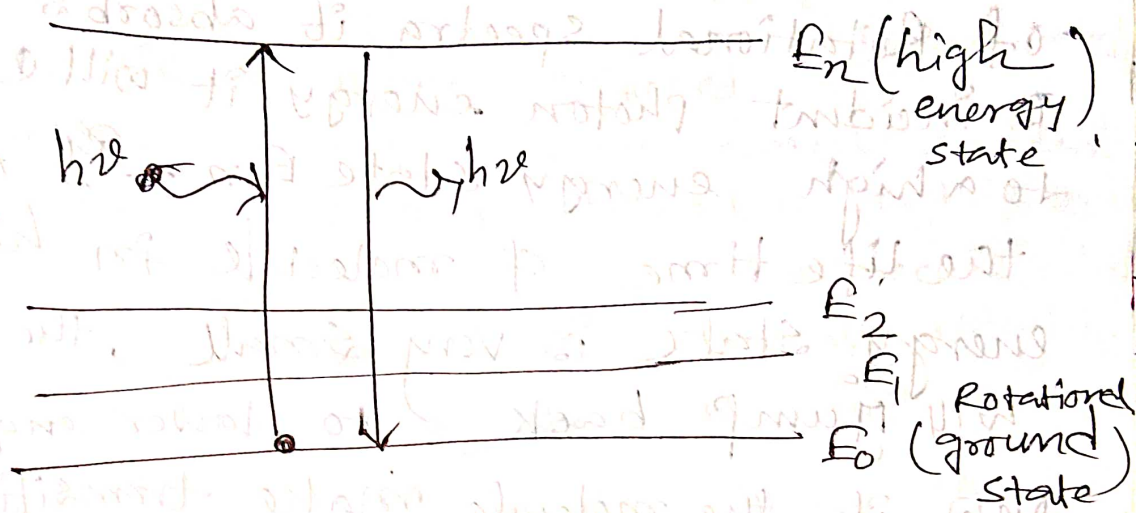
Explanation :-

We consider a dust free medium with transparent material, a monocromatic beam of light incident on the medium. The maximum portion of the incident light passes through the medium without any deflection. A small portion of light is scattered by the medium. In scattered light, there are three type's of wave length present — the original frequency of incident photon, the frequency less than the frequency of incident photons, the frequency greater than the frequency of incident photon —.



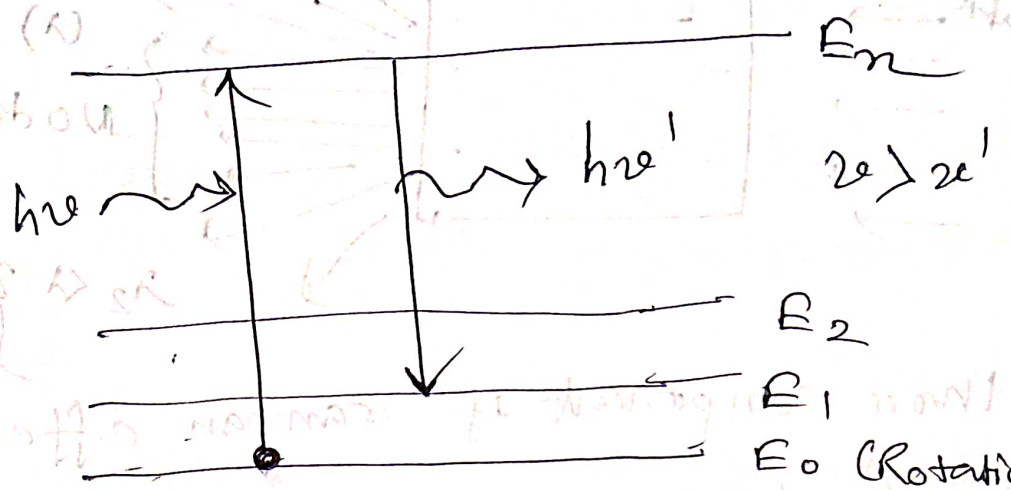

the three component of raman effect ——

(i) Rayleigh scattering :-




If a molecule in the ground state of Rotational spectra absorbs the incident photon energy, it will exited to a high energy level $E_n$. As the life time of a molecule is very less in higher exited state, the molecule jump back to the rotational ground state by emitting a photon of frequency equal to the frequency of incident photon this type of scattering is known as Rayleigh scattering. In rayligh scattering there is no change in wavelength y i.e. scattered photon frequency equal to incident photon frequency.

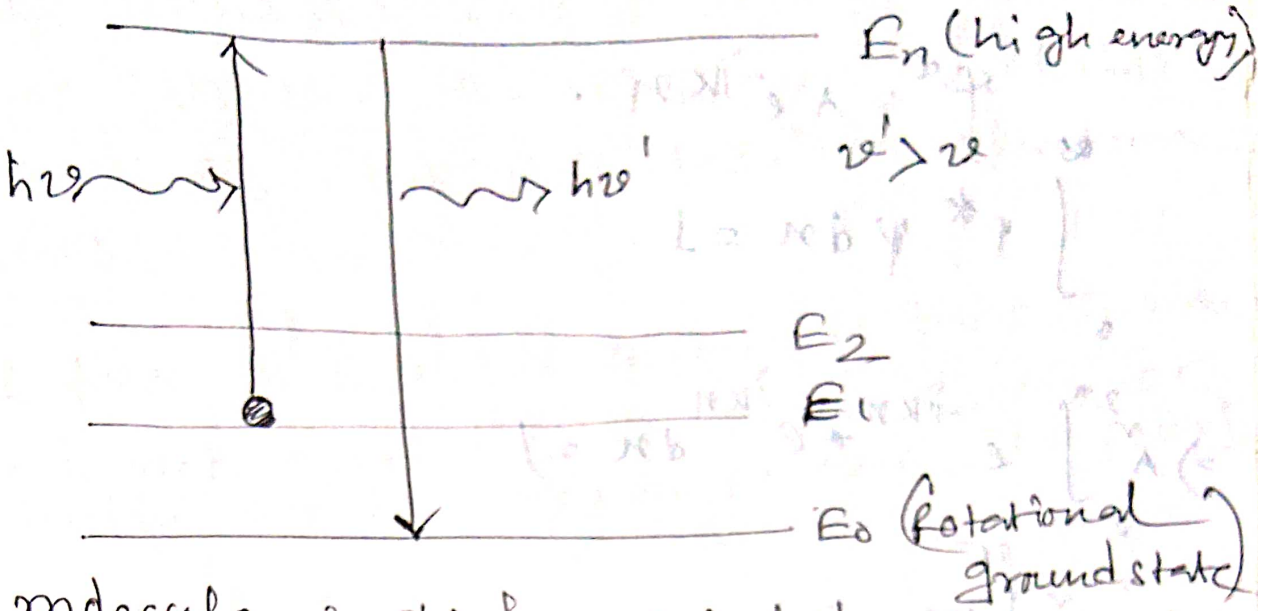
(ii) Stokes line/scattering :-




If a molecule in Rotational ground state of Rotational spectra it absorb's the incident photon energy it will excited to a high energy state $E_n$. As the life time of molecule in high energy state is very small, the molecule will jump back to lower engy state. Now if the molecule make transition to any energy level except ground state, the frequency of emitted photon is less than the frequency of incident photon. This is known as stoke's scattering Stoke's line.

In stokes scattering, scattered photon frequency is less than incident photon frequency.

(iii) Anti-stokes scattering :-




If a molecule in higher exicted state of rotational spectra absorbs incident photon energy, it will make transition to higher energy level. As the lifetime of molecule in Higher exited state is very small it will jump back to ground state by emitting photon of freqeency greater than the frequency of incident photon. This is known as antistoke's scattering.

In Antistokes scattering, scattered photon frqeeney is greater than incident photon frequeney. Antistoke's scattering is very rare phenomenone scattering.

The intensity order of rayleigh scattrin, stokes' scattering, antistokes scattering is given by, $I_{rayleigh} > I_{stokes} > I_{antistokes}$

$$\psi = A e^{ikx}$$

$$\psi^* = A e^{-ikx}.$$

$$\int_0^{\infty} \psi^* \psi \, dx = 1$$

$$\Rightarrow A^2 \int_0^{2\pi} e^{-ikx} \cdot e^{ikx} \, dx = 1$$

$$\Rightarrow A^2 \int_0^{2\pi} dx = 1$$

$$\Rightarrow A^2 = \frac{1}{2\pi}$$

$$\Rightarrow A = \sqrt{2\pi}$$

$$\psi = \frac{1}{\sqrt{2\pi}} e^{ikx}$$

(1) → If the Probability density $\rho = \psi^* \psi$ for any considered wave function $\psi$ is independent of time, then this kind of wave fun$^n$ is known as Stationary state in quantum Mechanics.

(2) → A free particle is a particle that, in some sense, is not bound by an external force, or equivalently not in a region where its potential energy varies.

(3) → At absolute zero temp. ($T = 0K$) the system has minimum energy, then this energy is known as zero point energy.

The zero point energy for harmonic oscillator is $\frac{\hbar\omega}{2}$.

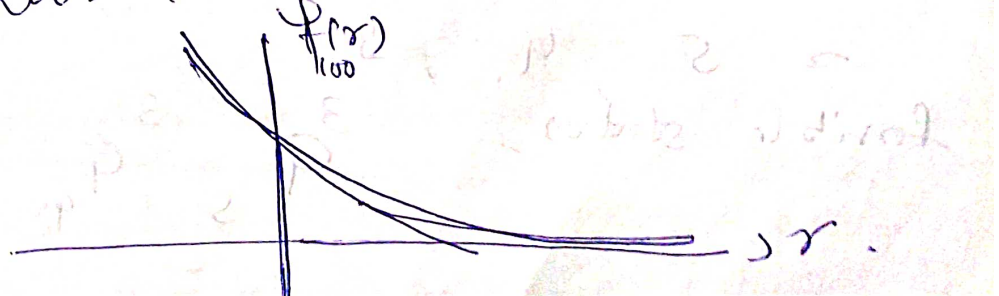
Significance → according to uncertainity principle,

$$\Delta E \Delta t \geq \frac{\hbar}{2}$$

at, $\Delta E \to 0$, $\Delta t \to \infty$.

Physically which is not acceptable. So, the system must have a minimum energy, which is known as zero point energy.

(4) →



→ $3p^1$ , $4f^1$

For 1st $e^-$ : $l_1 = 1$, $s_1 = \frac{1}{2}$

For 2nd $e^-$ : $l_2 = 3$, $s_2 = \frac{1}{2}$

## Orbital - orbital coupling (L-L)

$l_1 = 1$, $l_2 = 3$

$\therefore L = |l_1 + l_2| \cdots\cdots |l_1 - l_2|$

$= 4, 3, 2$

## Spin - spin coupling (S-S)

$s_1 = \frac{1}{2}$, $s_2 = \frac{1}{2}$

$\therefore S = |s_1 + s_2| \cdots\cdots |s_1 - s_2|$

$= 1, 0$

## L-S coupling

$L = 4$, $S = 1$,

$J = |L + S| \cdots |L - S|$

$= 5, 4, 3$

Possible states - $^3G_5$ , $^3G_4$ , $^3G_3$

$l = 4, \quad S = 0$

$J = 4$

Possible states, $^1G_4$,

$l = 3, \quad S = 1$

$J = 4, 3, 2$

Possible state $^3F_4, {}^3F_3, {}^3F_2$.

$l = 3, \quad S = 0$

$J = 3.$

Possible state, $^1F_3$

$l = 2, \quad S = 1$

$J = 3, 2, 1$

Possible states, $^3D_3, {}^3D_2, {}^3D_1$

$l = 2, \quad S = 0$

$J = 2$

Possible state, $^1D_2$

(b) J-J coupling.

Spin-orbit coupling for ($1^{st}$ $e^-$)

$l_1 = 1, \quad s_1 = 1/2$

$J_1 = |l_1 + s_1| \quad \cdots \quad |l_1 - s_1| = 3/2, \ 1/2.$

## Spin - Orbit coupling (cont'd)

$l_2 = 3, \quad s_2 = \frac{1}{2}.$

$\therefore j_2 = 7/2 \;,\; 5/2$

9. **J - J coupling**

$j_1 = 3/2, \; j_2 = 7/2$

$j = |j_1 + j_2| \cdots |j_1 - j_2|$

$= 5, 4, 3, 2$

$\therefore$ Possible state $(3/2, 7/2)_{5,4,3,2}$.

**$j_1 = 3/2, \; j_2 = 5/2$**

$j = 4, 3, 2, 1$

$\therefore$ Possible state $(3/2, 5/2)_{4,3,2,1}$.

**$j_1 = 1/2 \;.\; j_2 = 7/2$**

$j = 4, \quad 3$

$\therefore$ Possible, state $(1/2, 7/2)_{4,3}$.

**$j_1 = 1/2, \; j_2 = 5/2$**

$j = 3, \quad 2.$

$\therefore$ Possible state: $(1/2, 5/2)_{3,2}$.

(e) Larmor's theorem:- It's state that, when an atom is placed in a external magnetic field, the orbit precesses about the direction of the applied magnetic field. due to the torque applied on the atom.

(f) the spliting of spectral line in precence of strong electric field is known as stark effect.

(g) $Mg^{12} \longrightarrow 1s^2\ 2s^2\ 2p^6\ 3s^2$

for full filled shell the ground state will be $^1S_0$

$3S^2 \longrightarrow l = 0, S = \frac{1}{2}, -\frac{1}{2}$

$l_1 = 0, S_1 = \frac{1}{2}$

$\therefore J_1 = |l_1 + S_1| \cdots\cdots |l_1 - S_2|$

$= \frac{1}{2}$

$\therefore$ Possible state's are $^2S_{1/2}$

$l_2 = 0, S_2 = -\frac{1}{2}$.

$\therefore J_2 = |l_2 + S_2| \cdots\cdots |l_2 - S_2|$

$= \frac{1}{2}$

$\therefore$ Possible state are $^2S_{1/2}$

for. $3s^2$, $l = 0, S = 0$.

$J = |(l+s) \cdots |l-s| = 0$

$\therefore$ the possible state $= {}^{2s+1}S_0 = {}^1S_0$

(4) $2\,^2S_{1/2}$ , $3\,^2P_{1/2}$.

(i) $3\,^2S_{1/2}$

Here, $2S+1 = 2$

$\Rightarrow S = 1/2$,

$L = 0$,

$J = 1/2$.

$\therefore g = 1 + \dfrac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$

$= 1 + \dfrac{\frac{1}{2}(1+\frac{1}{2}) + \frac{1}{2}(1+\frac{1}{2}) - 0}{2\,\frac{1}{2}(\frac{1}{2}+1)}$

$= 1 + \dfrac{\frac{3}{4} + \frac{3}{4}}{2 \times \frac{3}{4}}$

$= 1 + \dfrac{6/4}{6/4}$

$= 1 + 1$

$= 2$

(ii) $3\,^1P_{1/2}$ Here, $2S+1 = 2$

$\Rightarrow S = 1/2$,

$L = 1$,

$J = 1/2$

$\therefore g = 1 + \dfrac{\frac{1}{2}(\frac{1}{2}+1) + \frac{1}{2}(\frac{1}{2}+1) - 2}{2 \cdot \frac{1}{2}(1+\frac{1}{2})}$

$= 1 + \dfrac{\frac{3}{4} + \frac{3}{4} - 2}{\frac{6}{4}}$

$= 1 + \dfrac{6-8}{6}$

$= 1 - \frac{1}{3}$

$g = \frac{2}{3}$ Ans.

(5)

(a)(i) Pauli exclusion Principle:- The Principle states that, two or more identical particle with half-integer spins cannot occupy the same quantum state simultaneously.

(ii) $N^{11} \longrightarrow 1s^2\ 2s^2\ 2p^6\ 3s^1$

(iii) Given, $l_1 = 1, \quad l_2 = 3.$

$\therefore$ Possible value of $L_1 = \sqrt{l_1(l_1+1)}\,\hbar$

$= \sqrt{1\cdot(2)}\,\hbar$

$= \sqrt{2}\,\hbar$

$\therefore$ Possible value of $L_2 = \sqrt{l_2(l_2+1)}\,\hbar$

$= \sqrt{3(3+1)}\,\hbar$

$= 2\sqrt{3}\,\hbar$ Ans.

(iv) For $^1S_0$,

$\because 2S+1 = 1, \quad l = 0, \quad j = 0$

$\therefore S = 0,$

$\therefore S = \sqrt{s(s+1)}\,\hbar = 0,$

$L = \sqrt{l(l+1)}\,\hbar = 0,$

$J = \sqrt{j(j+1)}\,\hbar = 0.$

For, $^3P_2$

$2S+1 = 3$, $L = 1$, $J = 2$

$\Rightarrow S = 1$

$\therefore S = \sqrt{S(S+1)}\hbar = \sqrt{2}\hbar$

$L = \sqrt{l(l+1)}\hbar = \sqrt{2}\hbar$

$J = \sqrt{j(j+1)}\hbar = \sqrt{6}\hbar$.

For, $^2D_{3/2}$

$2S+1 = 2$

$\Rightarrow S = 1/2$, $l = 2$, $j = 3/2$.

$\therefore S = \sqrt{s(s+1)}\hbar = \frac{\sqrt{3}}{2}\hbar$

$L = \sqrt{l(l+1)}\hbar = \sqrt{6}\hbar$

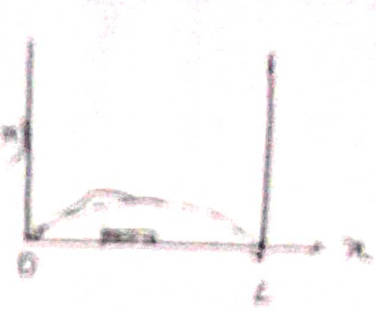
$J = \sqrt{j(j+1)}\hbar = \frac{\sqrt{15}}{2}\hbar$

(ii) Ground state electronic configuration of H-atom is $1s^1$.

So, It has one $e^-$, in 's' state, In which there is no orbital angular momentum i.e. $l = 0$, $s = \frac{1}{2}$.

Depending upon the orientation of it's spin vector s, for single $e^-$ $s = \frac{1}{2}$, so, only one sub state will exist, that's why can't split into two levels.

# Perturbation Theory:-

$$\psi_n(x) = \psi_n^{(0)}(x) + \psi_n^{(1)}(x) + \psi_n^{(2)}(x)$$

- $\psi_n^{(0)}(x)$ → Wave fun$^n$ of Unperturbed state
- $\psi_n^{(1)}(x)$ → 1st order correction